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⑮ Fuel compositions and additive concentrates, and their use in inhibiting engine coking.

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## Description

The invention relates to compression ignition fuel compositions and additive mixtures of organic nitrate ignition accelerator and hydrocarbyl-substituted succinimide or succinamide, in amounts sufficient to resist the coking tendencies of compression ignition fuel compositions when used in the operation of indirect injection diesel engines.

Throttling diesel nozzles have recently come into widespread use in indirect injection automotive and light-duty diesel truck engines, i.e., compression ignition engines in which the fuel is injected into and ignited in a prechamber or swirl chamber. In this way, the flame front proceeds from the prechamber into the larger compression chamber where the combustion is completed. Engines designed in this manner allow for quieter and smoother operation. The Figure of the Drawing illustrates the geometry of the typical throttling diesel nozzle (often referred to as the "pintle nozzle").

Unfortunately, the advent of such engines has given rise to a new problem, that of excessive coking on the critical surfaces of the injectors that inject fuel into the prechamber or swirl chamber of the engine. In particular, and with reference to the accompanying Figure, the carbon tends to fill in all of the available corners and surfaces of the obturator 10 and the form 12 until a smooth profile is achieved. The carbon also tends to block the drilled orifice 14 in the injector body 16 and fill up to the seat 18. In severe cases, carbon builds up on the form 12 and the obturator 10 to such an extent that it interferes with the spray pattern of the fuel issuing from around the perimeter of orifice 14. Such carbon build up or coking often results in such undesirable consequences as delayed fuel injection, increased rate of fuel injection, increased rate of combustion chamber pressure rise, and increased engine noise, and can also result in an excessive increase in emission from the engine of unburned hydrocarbons.

While low fuel cetane number is believed to be a major contributing factor to the coking problem, it is not the only relevant factor. Thermal and oxidative stability (lacquering tendencies), fuel aromaticity, and such fuel characteristics as viscosity, surface tension and relative density have also been indicated to play a role in the coking problem.

An important contribution to the art would be a fuel composition which has enhanced resistance to coking tendencies when employed in the operation of indirect injection diesel engines.

This invention provides distillate fuel for indirect injection compression ignition engines containing a combination of (a) organic nitrate ignition accelerator, and (b) hydrocarbyl-substituted succinimide or succinamide, and optionally:

(c) hydrocarbyl amine having from 3 to 60 carbons and from 1 to 10 nitrogens, or  
 a combination of the hydrocarbyl amine (c) and (d) N,N'-disalicylidene-1,2-diaminopropane,  
 the combination being present in an amount sufficient to suppress and preferably to minimize coking,  
 especially throttling nozzle coking, in the prechambers or swirl chambers of indirect injection compression ignition engines operated on such fuel.

Included in the invention is additive fluid concentrate for use in distillate fuels and which contains a combination defined above.

Since the invention also embodies the operation of an indirect injection compression ignition engine in a manner which results in reduced coking, a still further embodiment of the present invention is a method of inhibiting coking, especially throttling nozzle coking, in the prechambers or swirl chambers of an indirect injection compression ignition engine, which comprises supplying said engine with a distillate fuel containing a combination as defined above, said combination being present in an amount sufficient to minimize such coking in an engine operated on such fuel.

A feature of this invention is that the combination of additives utilized in its practice is capable of suppressing coking tendencies of fuels used to operate indirect injection compression ignition engines. Such behavior was exhibited in a series of standard engine dynamometer tests conducted as described in Examples I, II and III hereinafter.

A wide variety of organic nitrate ignition accelerators, component (a), may be employed in the fuels of this invention. Preferred nitrate esters are the aliphatic or cycloaliphatic nitrates in which the aliphatic or cycloaliphatic group is saturated, contains up to about 12 carbons and, optionally, may be substituted with one or more oxygen atoms.

Typical organic nitrates that may be used are methyl nitrate, ethyl nitrate, propyl nitrate, isopropyl nitrate, allyl nitrate, butyl nitrate, isobutyl nitrate, sec-butyl nitrate, tert-butyl nitrate, amyl nitrate, isoamyl nitrate, 2-amyl nitrate, 3-amyl nitrate, hexyl nitrate, heptyl nitrate, 2-heptyl nitrate, octyl nitrate, isoocetyl nitrate, 2-ethylhexyl nitrate, nonyl nitrate, decyl nitrate, undecyl nitrate, dodecyl nitrate, cyclopentyl nitrate, cyclohexyl nitrate, methylcyclohexyl nitrate, cyclododecyl nitrate, 2-ethoxyethyl nitrate, 2-(2-ethoxyethoxyethyl nitrate, tetrahydrofurenanyl nitrate, and the like. Mixtures of such materials may also be used. The preferred ignition accelerator for use in the fuels of this invention is a mixture of octyl nitrates available as an article of commerce from Ethyl Corporation under the designation DII-3 Ignition Improver.

The hydrocarbyl-substituted succinimides, component (b) of the fuels of this invention, are well known. They are readily made by first reacting an olefinically unsaturated hydrocarbon of the desired molecular weight with maleic anhydride to form a hydrocarbyl-substituted succinic anhydride. Reaction temperatures of 100-250°C are used. With higher boiling olefinically-unsaturated hydrocarbons, good results are obtained at 200-250°C. This reaction can be promoted by the addition of chlorine. Typical

olefins include cracked wax olefins, linear alpha olefins, branched chain alpha olefins, polymers and copolymers of lower olefins. These include polymers of ethylene, propylene, isobutylene, 1-hexene, 1-decene and the like. Useful copolymers are ethylene-propylene copolymers, ethylene-isobutylene copolymers, propylene-isobutylene copolymers, ethylene-1-decene copolymers and the like.

5 Hydrocarbyl substituents have also been made from olefin terpolymers. Very useful products have been made from ethylene-C<sub>3</sub>-12 alpha olefin - C<sub>3</sub>-12 non-conjugated diene terpolymers; such as ethylene-propylene-1,4-hexadiene terpolymer; ethylene-propylene-1,5-cyclooctadiene terpolymer; ethylene-propylene-norbornene terpolymers and the like.

10 Of the foregoing, by far the most useful hydrocarbyl substituents are derived from butene polymers, especially polymers of isobutylene.

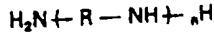
The molecular weight of the hydrocarbyl substituent can vary over a wide range. It is desirable that the hydrocarbyl group have a molecular weight of at least 500. Although there is no critical upper limit, a preferred range is 500-500,000 number average molecular weight. The more preferred average molecular weight is 700-5,000 and most preferably 900-3,000.

15 Hydrocarbyl-substituted succinimides and succinamides are made by reaction of the desired hydrocarbyl-substituted succinic anhydride with an amine having at least one reactive hydrogen atom bonded to an amine nitrogen atom. Examples of these are methyl amine, dimethyl amine, n-butyl amine, di-(n-dodecyl) amine, N-(aminoethyl) piperidine, piperazine, N-(3-aminopropyl) piperazine, and the like.

20 Preferably, the amine has at least one reactive primary amine group capable of reacting to form the preferred succinimides. Examples of such primary amines are n-octyl amine, N,N-dimethyl-1,3-propane diamine, N-(3-aminopropyl) piperazine, 1,6-hexane diamine, and the like.

25 Hydroxylalkyl amines can also be used to make the succinimide-succinamide components of the invention which contain some ester groups. These amines include ethanol amine, diethanol amine, 2-hydroxypropyl amine, N-hydroxyethyl ethylenediamine and the like. Such hydroxylalkyl amines can be made by reacting a lower alkylene oxide, such as ethylene oxide, propylene oxide or butylene oxide with ammonia or a primary or secondary amine such as ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylenepentamine and the like.

30 A more preferred class of primary amines used to make the succinimide, succinamide or mixtures thereof are the polyalkylene amines. These are polyamines and mixtures of polyamines which have the general formula



35 wherein R is a divalent aliphatic hydrocarbon group having 2-4 carbon atoms and n is an integer from 1-10 including mixtures of such polyalkylene amines.

40 In a highly preferred embodiment, the polyalkylene amine is a polyethylenamine containing 2-6 ethylenearmine units. These are represented by the above formula in which R is the group -CH<sub>2</sub>CH<sub>2</sub>- and n has a value of 2-6.

The amine used to make the succinimide, succinamide or mixture thereof need not be all amine. A mono or poly-hydroxylalcohol may be included in the reaction. Such alcohols can be reacted concurrently with the amine or the two alcohol and amine may be reacted sequentially. Useful alcohols are methanol, ethanol, n-dodecanol, 2-ethyl hexanol, ethylene glycol, propylene glycol, diethylene glycol, 2-ethoxy ethanol, trimethylol propane pentaerythritol, dipentaerythritol and the like.

45 Useful amine-alcohol products are described in U.S. 3,184,474; U.S. 3,576,743; U.S. 3,632,511; U.S. 3,804,763; U.S. 3,836,471; U.S. 3,936,480; U.S. 3,948,800; U.S. 3,950,341; U.S. 3,957,854; U.S. 3,957,855; U.S. 3,991,098; U.S. 4,071,548 and U.S. 4,173,540.

50 The reaction between the hydrocarbyl-substituted succinic anhydride and the amine can be carried out by mixing the components and heating the mixture to a temperature high enough to cause a reaction to occur but not so high as to cause decomposition of the reactants or products or the anhydride may be heated to reaction temperature and the amine added over an extended period. A useful temperature is 100-250°C. Best results are obtained by conducting the reaction at a temperature high enough to distill out water formed in the reaction.

55 A preferred succinimide-succinamide component is available as an article of commerce from the Edwin Cooper Company under the designation HITEC® E-644. This product comprises a mixture of active ingredients and solvent. Thus, when HITEC® E-644 is used as component (b) in formulating the fuels of this invention, the product as received should be used at a concentration of at least about 40 PTB (pounds per thousand barrels) - 0.11436 grams per liter - to insure that the finished blend contains an adequate quantity of the foregoing succinimide-succinamide ingredient although smaller amounts may be successfully employed.

60 The nitrate ignition accelerator-component (a) - should be present in an amount of at least 100 to 1000 PTB (pounds per thousand barrels) - 0.2859 to 2.859 grams per liter - of the base fuel. Preferably, the concentration of the ignition accelerator is 400 to 600 PTB (1.1436 to 1.7154 grams per liter).

65 It is not believed that there is anything critical as regards the maximum amount of components (a) and (b) used in the fuel. Thus, the maximum amount of these components will probably be governed in any given situation by matters of choice and economics.

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5 The coking-inhibiting components (a) and (b) of the invention can be added to the fuels by any means known in the art for incorporating small quantities of additives into distillate fuels. Components (a) and (b) can be added separately or they can be combined and added together. It is convenient to utilize additive fluid mixtures which consist of organic nitrate ignition accelerator and hydrocarbyl-substituted succinimide-succinamide agents. These additive fluid mixtures are added to distillate fuels. In other words, part of the present invention are coking inhibiting fluids which comprise organic nitrate ignition accelerator and hydrocarbyl-substituted succinimide-succinamide.

10 Such fluids in addition to resulting in great convenience in storage, handling, transportation, blending with fuels, and so forth, also are potent concentrates which serve the function of inhibiting or minimizing the coking characteristics of compression ignition distillate fuels used to operate indirect compression ignition engines.

15 In these fluid compositions, the amount of components (a) and (b) can vary widely. In general, the fluid compositions contain 5 to 95% by weight of the organic nitrate ignition accelerator component and 5 to 95% by weight of the hydrocarbyl-substituted succinimide-succinamide component. Typically, from .01% by weight up to 1.0% by weight of the combination will be sufficient to provide good coking-inhibiting properties to the distillate fuel. A preferred distillate fuel composition contains from 0.1 to 0.5% by weight of the combination containing from 25% to 95% by weight of the organic nitrate ignition accelerator and from 75% to 5% by weight of the hydrocarbyl-substituted succinimide-succinamide component.

20 The additive fluids, as well as the distillate fuel compositions of the present invention may also contain other additives such as, corrosion inhibitors, antioxidants, metal deactivators, detergents, cold flow improvers, inert solvents or diluents, and the like.

25 Accordingly, a more preferred distillate fuel composition includes a hydrocarbyl amine in combination with the present additives.

While a variety of hydrocarbyl amines may be used in the fuel compositions of this invention, a primary aliphatic amine, the aliphatic group of which is tertiary, e.g., an amine of the formula:



30 wherein R is one or a mixture of tertiary aliphatic groups containing 8 to 18 or more (preferably 12-16) carbon atoms is preferred. Most preferably, these tertiary aliphatic groups are tertiary alkyl groups. It is also preferred that hydrocarbyl amine component (c) include in addition to the above-described amine one or more hydrocarbyl amines differing therefrom.

35 U.S. Pat. No. 3,909,215 gives a description of the various hydrocarbyl amines having from 3 to 60 carbons and from 1 to 10 nitrogens which may be employed in the fuels of this invention. A few additional examples of desirable amines include 2,6-di-*tert*-butyl-*α*-dimethylamino-*p*-cresol, N-cyclohexyl-N,N-dimethylamine, and N-alkyl-N,N-dimethylamines in which the alkyl group is one or a combination of alkyl groups preferably having 8 to 18 or more carbon atoms.

40 A particularly preferred hydrocarbyl amine is available commercially from the Rohm and Haas Company under the designation Primene 81R. The Primene 81R is believed to be a mixture of primary aliphatic amines in which the aliphatic groups are predominantly C<sub>12</sub> and C<sub>14</sub> tertiary alkyl groups.

45 The fuels of this invention should contain at least 1.5 to 40 PTB (0.00429 to 0.1143 grams/liter of component (c), the hydrocarbyl amine.

50 Accordingly, another embodiment of the present invention is distillate fuel for indirect injection compression ignition engines containing a combination of (a) organic nitrate ignition accelerator, (b) hydrocarbyl-substituted succinimide, and (c) hydrocarbyl amine, said combination being present in an amount sufficient to minimize coking, especially throttling nozzle coking in the prechambers or swirl chambers in indirect injection compression ignition engines operated on such fuel.

55 Also included as a further embodiment of the invention is a distillate fuel additive concentrate comprising the combination of (a), (b) and (c).

60 In general, these additive fuel concentrates will contain as much as 50% by weight of the combination of organic nitrate ignition accelerator and hydrocarbyl-substituted succinimide and up to 50% of the hydrocarbyl amine or other additives when they are present.

65 In a still further embodiment of the invention there is provided a method of inhibiting coking, especially throttling nozzle coking in the prechambers or swirl chambers of an indirect injection compression ignition engine which comprises supplying said engine with a distillate fuel containing a combination of (a) organic nitrate ignition accelerator, (b) hydrocarbyl-substituted succinimide or succinamide and (c) hydrocarbyl amine, said combination being present in an amount sufficient to suppress and preferably to minimize such coking in an engine operated on such fuel.

70 Another additive which can be used to advantage in the present invention is the metal deactivator N,N'-disalicylidene-1,2-diaminopropane. This compound (80 weight percent active in 20 weight percent toluene solvent) is available as an article of commerce from Ethyl Corporation under the designation "Ethyl" MDA.

75 The fuels of this invention should contain at least 0.2 to 5 PTB (0.00572 to 0.012 grams per liter) of component (d), N,N'-disalicylidene-1,2-diaminopropane.

80 Accordingly, another embodiment of the present invention is distillate fuel for indirect injection

compression ignition engines containing a combination of (a) organic nitrate ignition accelerator, (b) hydrocarbyl-substituted succinimide or succinamide, (c) hydrocarbyl amine, and (d) N,N'-disalicylidene-1,2-diaminopropane, said combination being present in an amount sufficient to suppress and preferably to minimize coking, especially throttling nozzle coking in the prechambers or swirl chambers in indirect injection compression ignition engines operated on such fuel.

Also included as a further embodiment of the invention is a distillate fuel additive concentrate comprising the combination of (a), (b), (c) and (d).

In general, these additive fuel compositions will contain as much as 50% by weight of the combination of organic nitrate ignition accelerator and hydrocarbyl-substituted succinimide-succinamide and up to 50% of the combination of hydrocarbyl amine and N,N'-disalicylidene-1,2-diaminopropane or other additives when they are present.

In a still further embodiment of the invention there is provided a method of inhibiting coking, especially throttling nozzle coking in the prechambers or swirl chambers in an indirect injection compression ignition engine which comprises supplying said engine with a distillate fuel containing a combination of (a) organic nitrate ignition accelerator, (b) hydrocarbyl-substituted succinimide or succinamide, (c) hydrocarbyl amine and (d) N,N'-disalicylidene-1,2-diaminopropane, said combination being present in an amount to suppress and preferably to minimize such coking in an engine operated on such fuel.

The practice and advantages of this Invention will become still further apparent from the following illustrative Example.

20

#### Example 1

In order to determine the effect of the fuel compositions of the present invention on the coking tendency of diesel injectors in indirect injection compression ignition engines, use was made of a commercial diesel engine operated on a coking test cycle developed by Institute Francais Petrole and as practiced by Peugeot S. A. The amount of coking together with a quantitative indication of the adverse consequences of such coking was determined by means of (i) injector air flow performance, (ii) emission of unburned hydrocarbons, (iii) engine noise, and (iv) injector deposit ratings. The engine employed in the tests was a 1982 Peugeot 2.3 liter, 4-cylinder, turbocharged XD2S diesel engine connected to a Midwest dynamometer through an engine clutch. This engine is equipped with Bosch injectors positioned within prechambers, and is deemed representative of the indirect injection compression ignition engines widely used in automobiles and light-duty trucks.

The base fuel employed in these engine tests was a commercially-available diesel fuel having a nominal cetane rating of 42. FIA analysis indicated the fuel was composed by volume of 31.5% aromatics, 3.0% olefins and 65.5% saturates. Its distillation range (ASTM D-158) was as follows:

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	Barometer Initial % Evaporated	29.46 inches of Hg 406°F at °F	(0.9987 Bars) — 207.78°C at °C
5	5	439	226.11
	10	450	232.22
10	15	456	235.56
	20	463	239.44
15	30	480	248.89
	40	499	259.44
20	50	521	271.67
	60	545	285.0
25	70	572	300.0
	80	603	317.22
30	85	621	327.22
	90	643	339.44
35	95	678	358.89
	Final	678°F	358.89
40	Recovery	97.5%	
	Residue	2.5%	
45	Loss	None	
	Other inspection data on the base fuel were as follows:		
45	Kinematic Viscosity, (ASTM D—445)	3.50 Centistokes ( $3.5 \times 10^{-6} \text{ m}^2/\text{s}$ ), 40°C	
	Pour Point (ASTM D—97)	-26°C	
50	Cloud Point (ASTM D—97)	33°C	
	Flash Point (ASTM D—93)	91 °C	
55	Steam Jet Gum	2.4 mg/100 ml	
	Aniline Point (ASTM D—611)	143.4°F (61.89°C)	
60	Total Sulfur	0.41 wt. %	
	Ramsbottom Carbon, % (ASTM D—524)	0.1460 on 10%	
65	Residuum		
	Gravity (ASTM D—287)	31.8 °API	
65	Specific Gravity @ 25°C	0.86	
	Cetane rating	41	

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A test blend was prepared from this base fuel (Fuel A). Fuel A contained a combination of (i) 506 PTB (1.447 grams/liter) of mixed octyl nitrates (a commercial product available from Ethyl Corporation under the designation DII-3 Ignition Improver), (ii) 41 PTB (0.117 gram/liter) of HITEC® E-644, a product of Edwin Cooper, Inc., believed to be a hydrocarbyl succinimide-succinamide made by reacting two moles of 5 a polyisobutylene succinic anhydride (PIBSA) with one mole of a polyethylene amine mixture having an average composition corresponding to tetraethylene pentamine, (iii) 14 PTB (0.04 grams/liter) of a hydrocarbyl amine available commercially from Rohm and Haas Company under the designation Primene 81R and (iv) 1.7 PTB (0.00486 grams/liter) of "Ethyl" Metal Deactivator, a product of Ethyl Corporation, the active ingredient of which is N,N'-disalicylidene-1,2-diaminopropane. The manufacturer gives the 10 following typical properties for its HITEC® E-644 product:

	Appearance	Dark brown viscous liquid
15	Nitrogen, wt. %	2.0
	Specific Gravity at 60/60°F (15.6°C)	0.928
20	Viscosity at 210°F, (98.89°C)	340 cs ( $3.4 \times 10^{-4} \text{ m}^2/\text{s}$ )

The Primene 81R is believed to be a mixture of primary aliphatic amines in which the aliphatic groups are predominantly C<sub>12</sub> and C<sub>14</sub> tertiary alkyl groups. 25 The manufacturer gives the following typical properties for its "Ethyl" metal Deactivator:

	Form	liquid
	Color	Amber
30	Density, at 68°F (20°C) g/ml	1.0672
	lb/gal	8.91
35	Active ingredient, wt %	80
	Solvent vehicle (toluene), wt %	20
	Flash point, open cup, °F	84 (28.89°C)
40	Fire point, °F	100 (37.78°C)
	Solubility In gasoline (Typical)	Saturated solution contains 94% MDA
45	In water, wt. %	0.04

50 Shell Rotella T, an SAE 30, SF/CD oil was used as the crankcase lubricant. Before starting each test, new Bosch DNO SD — 1510 nozzles were installed using new copper gaskets and flame rings. The fuel line was flushed with the new test fuel composition to be tested and the fuel filter bowl and fuel return reservoir were emptied to avoid additive carry-over from test-to-test. At the start of each test, the engine was operated at 1000 rpm, light load for 15 minutes. After this warm-up, the engine was subjected to the following automatic cycle:

	Event	RPM	Beam Load	Minutes	EGR
55	1	750	0	4	off
60	2	2750	12.0	6	on
	3	1500	6.2	6	on
65	4	4000	16.2	4	off

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The above 20-minute cycle was repeated 60 times and the test was completed by running the engine at idle for another 30 minutes. The total elapsed time was thus 20.5 hours per test.

When passing from one event to the next event in the above cycle, some time, of course, was required to enable the engine to accelerate or decelerate from one speed to the next. Thus, more specifically, the above cycle was programmed as follows:

	Segment	Seconds	rpm	Beam Load
10	1	2	750	0
	2	200	750	0
	3	3*	2600	12
15	4	7*	2750	12
	5	350	2750	12
	6	3*	2275	6.2
20	7	7*	1500	6.2
	8	330	1500	6.2
	9	3*	3500	16.2
25	10	7*	4000	16.2
	11	230	4000	16.2
	12	3*	2000	0
30	13	7*	750	0
	14	30	750	0

\* Represents two mode periods for acceleration or deceleration to the next condition.

40 Hydrocarbon exhaust emissions were measured at the start of each test (after the first 20-minute cycle), at the 6-hour test interval and at the end of the test. These measurements were made at 750, 1000, and 1400 rpm idle. Noise level readings were made at a location three feet from the engine exhaust side. The measurements were made at the start and at the end of the test while operating at three idle speeds, viz., 750, 1000 and 1400 rpm.

45 After the test operation, the injectors were carefully removed from the engine so as not to disturb the deposits formed thereon. Measurements were made of air flow through each nozzle at different pintle lifts, and pintle deposits were rated using the CRC deposit rating system.

The most significant test results are given in Table I, in which air flow is expressed as cc/min and hydrocarbon emissions as ppm.

60 TABLE I

55	Fuel	Air Flow @ 0.1 mm Lift	Pintle Obturator Deposits (10 = clean)	Noise, DB		Hydrocarbon Emissions	
				EOT*	INCR.	EOT*	INCR.
	Base	36	8.0	83.8	3.0	577	406
	A	38	8.6	81.4	1.9	275	143

60 \* Value at end of test; the increase (Incr.) shown is in comparison to the value at start of test.

The results presented in Table I show that there were less coking deposits (higher air flow rate and fewer deposits), less engine noise and less hydrocarbon emissions with Fuel A, the fuel of the invention, as compared to the Base Fuel.

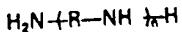
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In our European application 87 201 460.0 (EP-A-247706), divided out of the application forming the basis of the present patent, it is disclosed that coking in and around the injector nozzles of indirect injection compression ignition engines can be reduced by means of distillate fuel into which has been blended suitable concentrations of:

- 5 (a) organic nitrate ignition accelerator,  
(b) hydrocarbyl amine having from 3 to 60 carbons and from 1 to 10 nitrogens, and  
(c) N,N'-disalicylidene-1,2-diaminopropane.
- 10 Our European application 87 201 461.8 (EP-A-251419), also divided out of the application forming the basis of the present patent, discloses that coking in and around the injector nozzles of indirect injection compression ignition engines can be reduced by means of distillate fuel into which has been blended suitable concentrations of:  
(a) hydrocarbyl-substituted succinimide or succinamide.  
(b) hydrocarbyl amine having from 3 to 60 carbons and from 1 to 10 nitrogens, and  
(c) N,N'-disalicylidene-1,2-diaminopropane.

15 **Claims for the Contracting States: BE CH DE FR GB IT LI LU NL SE**

- 1 A distillate fuel composition for indirect injection compression ignition engines containing in an amount sufficient to suppress and preferably to minimize coking in nozzles of indirect injection compression ignition engines operated on such fuel a combination of (a) organic nitrate ignition accelerator and (b) hydrocarbyl-substituted succinimide or succinamide, and optionally:
  - (c) hydrocarbyl amine having from 3 to 60 carbons and from 1 to 10 nitrogens, or
  - a combination of the hydrocarbyl amine (c) and (d) N,N'-disalicylidene-1,2-diaminopropane.
- 2 A composition as claimed in claim 1, wherein the said ignition accelerator is a mixture of octyl nitrates.
- 3 A composition as claimed in claim 1 or claim 2, wherein said hydrocarbyl-substituted succinimide is an olefin polymer substituted succinimide wherein said olefin polymer substituent has an average molecular weight of 500-500,000.
- 4 A composition as claimed in claim 3, wherein olefin polymer substituent is a polyisobutene substituent having an average molecular weight of 700-5,000.
- 5 A composition as claimed in claim 3 or claim 4, wherein the succinimide portion is derived from a polyalkyleneamine having the formula



35 wherein R is a divalent aliphatic hydrocarbon group having 2-4 carbon atoms and n is an integer from 1-10 including mixtures of said polyalkylene amines.

- 6 A composition as claimed in claim 5, wherein said polyalkyleneamine is a polyethyleneamine having 2-6 ethylene amine units.
- 7 A composition as claimed in any one of claims 1 to 6 containing in an amount sufficient to suppress and preferably to minimize coking on the nozzles of indirect injection compression ignition engines operated on such fuel at least the combination of (a) organic nitrate ignition accelerator, (b) hydrocarbyl-substituted succinimide or succinamide, and (c) hydrocarbyl amine having from 3 to 60 carbons and from 1 to 10 nitrogens.
- 8 A composition as claimed in claim 7 also containing (d) N,N'-disalicylidene-1,2-diaminopropane.
- 9 An additive fluid concentrate for use in distillate fuels which contains a combination defined in any one of claims 1 to 8.
- 10 A method of inhibiting coking on the injector nozzles of an indirect injection compression ignition engine during operation thereof, which method comprises supplying said engine with a distillate fuel composition containing in an amount sufficient to suppress and preferably to minimize such coking in the engine operated on such fuel a combination defined in any one of claims 1 to 8.

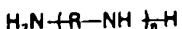
**Claims for the Contracting State: AT**

- 55 1. A process for preparing a distillate fuel composition for indirect injection compression ignition engines, which process comprises incorporating in distillate fuel in an amount sufficient to suppress and preferably to minimize coking in the nozzles of indirect injection compression ignition engines operated on such fuel a combination of (a) organic nitrate ignition accelerator and (b) hydrocarbyl-substituted succinimide or succinamide, and optionally:
  - (c) hydrocarbyl amine having from 3 to 60 carbons and from 1 to 10 nitrogens, or
  - a combination of the hydrocarbyl amine (c) and (d) N,N'-disalicylidene-1,2-diaminopropane.
- 60 2. A process as claimed in claim 1, wherein said ignition accelerator is a mixture of octyl nitrates and/or said hydrocarbyl-substituted succinimide is an olefin polymer substituted succinimide wherein said olefin polymer substituent has an average molecular weight of 500-500,000.

3. A process as claimed in claim 2, wherein said olefin polymer substituent is a polyisobutene substituent having an average molecular weight of 700-5,000.

4. A process as claimed in claim 2 or claim 3, wherein the succinimide portion is derived from a polyalkyleneamine having the formula

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wherein R is a divalent aliphatic hydrocarbon group having 2-4 carbon atoms and n is an integer from 1-10, including mixtures of said polyalkylene amines.

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5. A process as claimed in claim 4, wherein said polyalkyleneamine is a polyethyleneamine having 2-6 ethylene amine units.

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6. A process as claimed in any one of claims 1 to 5, wherein said fuel has incorporated therein in an amount sufficient to suppress and preferably minimize coking on the nozzles of indirect injection compression ignition engines operated on such fuel at least the combination of (a) organic nitrate ignition accelerator, (b) hydrocarbyl-substituted succinimide or succinamide and (c) hydrocarbyl amine having from 3 to 60 carbons and from 1 to 10 nitrogens.

7. A process as claimed in claim 6, wherein, in addition to components (a), (b) and (c), N,N'-disalicylidene-1,2-diaminopropane (d) is incorporated in said fuel.

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8. A process for preparing an additive fluid concentrate for use in distillate fuels, comprising formulating together the components of a combination as defined in any one of claims 1 to 7.

9. A method for inhibiting coking on the injector nozzles of indirect injection compression ignition engines during operation thereof, which method comprises supplying said engine with a distillate fuel composition containing in an amount sufficient to suppress and preferably to minimize coking in nozzles of indirect injection compression ignition engines operated on such fuel a combination of (a) organic nitrate ignition accelerator and (b) hydrocarbyl-substituted succinimide or succinamide, and optionally:

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(c) hydrocarbyl amine having from 3 to 60 carbons and from 1 to 10 nitrogens, or  
 a combination of the hydrocarbyl amine (c) and (d) N,N'-disalicylidene-1,2-diaminopropane, said combination optionally being as further defined in any one of claims 2 to 7.

10. The use as a distillate fuel additive to inhibit coking on the injector nozzles of indirect compression ignition engines of a combination of (a) organic nitrate ignition accelerator and (b) hydrocarbyl-substituted succinimide or succinamide, and optionally:

(c) hydrocarbyl amine having from 3 to 60 carbons and from 1 to 10 nitrogens, or  
 a combination of the hydrocarbyl amine (c) and (d) N,N'-disalicylidene-1,2-diaminopropane, the combination optionally being as further defined in any one of claims 2 to 7.

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Patentansprüche für die Vertragsstaaten: BE CH DE FR GB IT LI LU NL SE

1. Destillatölzusammensetzung für Kompressionszündungsmotoren mit Indirekter Einspritzung, die in einer Menge, die ausreicht, um das Vorkochen in Düsen von mit einem solchen Brennstoff betriebenen Kompressionszündungsmotoren mit indirekter Einspritzung zu unterdrücken und vorzugsweise zu minimieren, eine Kombination enthält von (a) organischem Nitrat-Zündungsbeschleuniger und (b) Hydrocarbyl-substituiertem Succinimid oder Succinamid, und gegebenenfalls:

(c) Hydrocarbylamin mit 3 bis 60 Kohlenstoffatomen und 1 bis 10 Stickstoffatomen, oder  
 einer Kombination des Hydrocarbylamins (c) und (d) N,N'-Disalicylidene-1,2-diaminopropan.

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2. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß der Zündungsbeschleuniger eine Mischung von Octylnitriten ist.

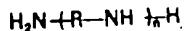
3. Zusammensetzung nach Anspruch 1 oder Anspruch 2, dadurch gekennzeichnet, daß das Hydrocarbyl-substituierte Succinimid ein Olefinpolymer-substituiertes Succinimid ist, worin der Olefinpolymer-Substituent ein mittleres Molekulargewicht von 500 bis 500 000 besitzt.

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4. Zusammensetzung nach Anspruch 3, dadurch gekennzeichnet, daß der Olefinpolymer-Substituent ein Polyisobutene-Substituent mit einem mittleren Molekulargewicht von 700 bis 5 000 ist.

5. Zusammensetzung nach Anspruch 3 oder Anspruch 4, dadurch gekennzeichnet, daß der Succinimidanteil abgeleitet ist von einem Polyalkylenamin mit der Formel

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worin R eine divalente aliphatische Kohlenwasserstoffgruppe mit 2 bis 4 Kohlenstoffatomen ist, und n eine ganze Zahl von 1 bis 10, einschließlich Mischungen dieser Polyalkylenamine.

6. Zusammensetzung nach Anspruch 5, dadurch gekennzeichnet, daß das Polyalkylenamin ein Polyethylenamin mit 2 bis 6 Ethylenamineinheiten ist.

7. Zusammensetzung nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß sie in einer Menge, die ausreicht, um das Vorkochen in Düsen von mit einem solchen Brennstoff betriebenen Kompressionszündungsmotoren mit indirekter Einspritzung zu unterdrücken und vorzugsweise zu minimieren, mindestens die Kombination von (a) organischem Nitrat-Zündungsbeschleuniger, (b)

65 (c) hydrocarbyl amine having from 3 to 60 carbons and from 1 to 10 nitrogens, or  
 a combination of the hydrocarbyl amine (c) and (d) N,N'-disalicylidene-1,2-diaminopropane, said combination optionally being as further defined in any one of claims 2 to 7.

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Hydrocarbyl-substituiertem Succinimid oder Succinamid, und (c) Hydrocarbylamin mit 3 bis 60 Kohlenstoffatomen und 1 bis 10 Stickstoffatomen enthält.

8. Zusammensetzung nach Anspruch 7, dadurch gekennzeichnet, daß sie außerdem (d) N,N'-Disalicyliden-1,2-diaminopropan enthält.

9. Flüssiges Zusatzkonzentrat zur Verwendung in Destillatölbrennstoffen, dadurch gekennzeichnet, daß es eine in einem der Ansprüche 1 bis 8 definierte Kombination enthält.

10. Verfahren zur Verhinderung des Verkokens an Injektordüsen eines Kompressionszündungsmotors mit indirekter Einspritzung während seines Betriebs, dadurch gekennzeichnet, daß man dem Motor eine Destillatölzusammensetzung zuführt, die in einer Menge, die ausreicht, um ein solches Verkoken in dem 10 mit einem solchen Brennstoff betriebenen Motor zu unterdrücken und vorzugsweise zu minimieren, eine in einem der Ansprüche 1 bis 8 definierte Kombination enthält.

Patentansprüche für den Vertragsstaat: AT

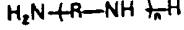
15 1. Verfahren zur Herstellung einer Destillatölzusammensetzung für Kompressionszündungsmotoren mit indirekter Einspritzung, dadurch gekennzeichnet, daß man in ein Destillatöl in einer Menge, die ausreicht, um das Verkoken in Düsen von mit einem solchen Brennstoff betriebenen Kompressionszündungsmotoren mit indirekter Einspritzung zu unterdrücken und vorzugsweise zu minimieren, eine Kombination einbringt von (a) organischem Nitrat-Zündungsbeschleuniger und (b) Hydrocarbyl-substituiertem Succinimid oder Succinamid, und gegebenenfalls:

20 (c) Hydrocarbylamin mit 3 bis 60 Kohlenstoffatomen und 1 bis 10 Stickstoffatomen, oder einer Kombination des Hydrocarbylamins (c) und (d) N,N'-Disalicyliden-1,2-diaminopropan.

25 2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß der Zündungsbeschleuniger eine Mischung von Octylnitrat und/oder das Hydrocarbyl-substituierte Succinimid ein Olefinpolymer-substituiertes Succinimid ist, worin der Olefinpolymer-Substituent ein mittleres Molekulargewicht von 500 bis 500 000 besitzt.

30 3. Verfahren nach Anspruch 2, dadurch gekennzeichnet, daß der Olefinpolymer-Substituent ein Polyisobuten-Substituent mit einem mittleren Molekulargewicht von 700 bis 5 000 ist.

4. Verfahren nach Anspruch 2 oder 3, dadurch gekennzeichnet, daß der Succinimid-Anteil abgeleitet ist von einem Polyalkylenamin mit der Formel



worin R eine divalente aliphatische Kohlenwasserstoffgruppe mit 2 bis 4 Kohlenstoffatomen ist, und n eine ganze Zahl von 1 bis 10, einschließlich Mischungen dieser Polyalkylenamine.

35 5. Verfahren nach Anspruch 4, dadurch gekennzeichnet, daß das Polyalkylenamin ein Polyethylenamin mit 2 bis 6 Ethylenamin-Einheiten ist.

6. Verfahren nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß in dem Brennstoff in einer Menge, die ausreicht, um das Verkoken in Düsen von mit einem solchen Brennstoff betriebenen Kompressionszündungsmotoren mit indirekter Einspritzung zu unterdrücken und vorzugsweise zu minimieren, mindestens die Kombination eingearbeitet ist von (a) organischem Nitrat-Hydrocarbylamin mit 3 bis 60 Kohlenstoffatomen und 1 bis 10 Stickstoffatomen.

40 7. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß zusätzlich zu den Komponenten (a), (b) und (c) N,N'-Disalicyliden-1,2-diaminopropan (d) in diesen Brennstoff eingearbeitet ist.

45 8. Verfahren zur Herstellung eines flüssigen Zusatzkonzentrats zur Verwendung in Destillatölbrennstoffen, dadurch gekennzeichnet, daß die Komponenten einer in einem der Ansprüche 1 bis 7 definierten Kombination gemeinsam formuliert werden.

9. Verfahren zur Verhinderung des Verkokens an den Injektordüsen von Kompressionszündungsmotoren mit indirekter Einspritzung während ihres Betriebes, dadurch gekennzeichnet, daß man dem Motor eine Destillatölzusammensetzung zuführt, die in einer Menge, die ausreicht, um das Verkoken in Düsen von mit einem solchen Brennstoff betriebenen Kompressionszündungsmotoren mit indirekter Einspritzung zu unterdrücken und vorzugsweise zu minimieren, eine Kombination enthält von (a) organischem Nitrat-Zündungsbeschleuniger und (b) Hydrocarbyl-substituiertem Succinimid oder Succinamid, und gegebenenfalls:

50 (c) Hydrocarbylamin mit 3 bis 60 Kohlenstoffatomen und 1 bis 10 Stickstoffatomen, oder einer Kombination des Hydrocarbylamins (c) und (d) N,N'-Disalicyliden-1,2-diaminopropan, wobei diese Kombination gegebenenfalls eine solche ist, wie sie weiters in einem der Ansprüche 2 bis 7 definiert ist.

55 10. Verwendung einer Kombination aus (a) organischem Nitrat-Zündungsbeschleuniger und (b) Hydrocarbyl-substituiertem Succinimid oder Succinamid, und gegebenenfalls:

60 (c) Hydrocarbylamin mit 3 bis 60 Kohlenstoffatomen und 1 bis 10 Stickstoffatomen, oder einer Kombination des Hydrocarbylamins (c) und (d) N,N'-Disalicyliden-1,2-diaminopropan, wobei die Kombination gegebenenfalls eine solche ist, wie sie weiters in einem der Ansprüche 2 bis 7 definiert ist, als Destillatölzusatz zur Verhinderung des Verkokens in Injektordüsen von indirekten Kompressionszündungsmotoren.

## Revendications pour les Etats contractants: BE CH DE FR GB IT LI LU NL SE

1. Composition de combustible distillé pour moteurs à allumage par compression à injection indirecte, contenant, en quantité suffisante pour supprimer et de préférence pour minimiser le dépôt de coke dans les injecteurs de moteurs à allumage par compression à injection indirecte fonctionnant avec un tel combustible, un mélange formé (a) d'un accélérateur d'allumage du type d'un nitrate organique et (b) d'un succinimide ou succinamide à substituant hydrocarbyle et, à titre facultatif:

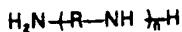
(c) une hydrocarbylamine de 3 à 60 atomes de carbone et 1 à 10 atomes d'azote, ou bien  
(d) une association de l'hydrocarbylamine (c) et (d) de N,N'-disalicylidène-1,2-diaminopropane.

2. Composition suivant la revendication 1, dans laquelle l'accélérateur d'allumage est un mélange de nitrates d'octyle.

3. Composition suivant la revendication 1 ou la revendication 2, dans laquelle le succinimide à substituant hydrocarbyle est un succinimide substitué par un polymère oléfinique, dont ledit substituant polymérique oléfinique a un poids moléculaire moyen de 500 à 500 000.

4. Composition suivant la revendication 3, dans laquelle le substituant polymérique oléfinique est un substituant polyisobutène ayant un poids moléculaire moyen de 700 à 5000.

5. Composition suivant la revendication 3 ou la revendication 4, dans laquelle la portion succinimide est dérivée d'une polyalkylène-amine répondant à la formule



dans laquelle R est un groupe hydrocarboné aliphatique divalent de 2 à 4 atomes de carbone et n est un nombre entier de 1 à 10, y compris des mélanges desdites polyalkylène-amines.

6. Composition suivant la revendication 5, dans laquelle la polyalkylène-amine est une polyéthylène-amine ayant 2 à 6 motifs éthylène-amine.

7. Composition suivant l'une quelconque des revendications 1 à 6, contenant, en une quantité suffisante pour supprimer et de préférence pour minimiser le dépôt de coke sur les injecteurs de moteurs à allumage par compression à injection indirecte fonctionnant avec un tel combustible, au moins l'association formée entre (a) un accélérateur d'allumage du type d'un nitrate organique, (b) un succinimide ou succinamide à substituant hydrocarbyle et (c) une hydrocarbylamine ayant 3 à 60 atomes de carbone et 1 à 10 atomes d'azote.

8. Composition suivant la revendication 7, contenant également (d) du N,N'-disalicylidène-1,2-diaminopropane.

9. Concentré liquide d'additif destiné à être utilisé dans des combustibles distillés, qui contient une association définie dans l'une quelconque des revendications 1 à 8.

10. Procédé pour inhiber le dépôt de coke sur les injecteurs d'un moteur à allumage par compression à injection indirecte pendant son fonctionnement, procédé qui consiste à alimenter ledit moteur avec une composition de combustible distillé contenant en une quantité suffisante pour supprimer et de préférence pour minimiser ce dépôt de coke dans le moteur utilisant ce combustible, une association définie suivant l'une quelconque des revendications 1 à 8.

## Revendications pour l'Etat contractant: AT

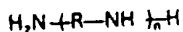
1. Procédé de préparation d'une composition de combustible distillé pour moteurs à allumage par compression à injection indirecte, procédé qui consiste à incorporer dans ledit combustible distillé, en une quantité suffisante pour supprimer et de préférence pour minimiser le dépôt de coke dans les injecteurs de moteurs à allumage par compression à injection indirecte utilisant un tel combustible, une association formée (a) d'un accélérateur d'allumage du type d'un nitrate organique et b) un succinimide ou succinamide à substituant hydrocarbyle, et à titre facultatif:

(c) une hydrocarbylamine ayant 3 à 60 atomes de carbone et 1 à 10 atomes d'azote, ou  
(d) une association formée de l'hydrocarbylamine (c) et (d) de N,N'-disalicylidène-1,2-diaminopropane.

2. Procédé suivant la revendication 1, dans lequel l'accélérateur d'allumage est un mélange de nitrates d'octyle et/ou ledit succinimide à substituant hydrocarbyle est un succinimide substitué par un polymère oléfinique, dont le substituant polymérique oléfinique a un poids moléculaire moyen de 500 à 500 000.

3. Procédé suivant la revendication 2, dans lequel le substituant polymérique oléfinique est un substituant polyisobutène ayant un poids moléculaire moyen de 700 à 5000.

4. Procédé suivant la revendication 2 ou la revendication 3, dans lequel la portion succinimide est dérivée d'une polyalkylène-amine répondant à la formule



dans laquelle R est un groupe hydrocarboné aliphatique divalent ayant 2 à 4 atomes de carbone et n est un nombre entier de 1 à 10, y compris des mélanges desdites polyalkylène-amines.

5. Procédé suivant la revendication 4, dans lequel ladite polyalkylène-amine est une polyéthylène-amine ayant 2 à 6 motifs éthylène-amine.

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6. Procédé suivant l'une quelconque des revendications 1 à 5, dans lequel est incorporée au combustible, en une quantité suffisante pour supprimer et de préférence pour minimiser le dépôt de coke sur les injecteurs de moteurs à allumage par compression à injection indirecte fonctionnant avec ce combustible, au moins l'association formée entre (a) un accélérateur d'allumage du type d'un nitrate organique, (b) un succinimide ou succinamide à substituant hydrocarbyle et (c) une hydrocarbylamine ayant 3 à 60 atomes de carbone et 1 à 10 atomes d'azote.

5 7. Procédé suivant la revendication 6, dans lequel du N,N-disalicylidène-1,2-diaminopropane (d) est incorporé dans le combustible, en plus des composants (a), (b) et (c).

8. Procédé de préparation d'un concentré liquide d'additif destiné à être utilisé dans des combustibles 10 distillés, qui consiste à formuler ensemble des composants d'une association telle que défini dans l'une quelconque des revendications 1 à 7.

9. Procédé pour inhiber le dépôt de coke sur les injecteurs de moteurs à allumage par compression à 15 injection indirecte pendant leur fonctionnement, procédé qui consiste à alimenter ledit moteur avec une composition de combustible distillé contenant, en une quantité suffisante pour supprimer et de préférence pour minimiser le dépôt de coke dans des injecteurs de moteurs à allumage par compression à injection indirecte fonctionnant avec un tel combustible, une association (a) d'un accélérateur d'allumage du type d'un nitrate organique et (b) d'un succinimide ou succinamide à substituant hydrocarbyle et, à titre facultatif:

20 (c) une hydrocarbylamine ayant 3 à 60 atomes de carbone et 1 à 10 atomes d'azote, ou bien une association formée de l'hydrocarbylamine (c) et (d) de N,N'-disalicylidène-1,2-diaminopropane, ladite association étant, à titre facultatif, telle que défini dans l'une quelconque des revendications 2 à 7.

10. Utilisation comme additif pour combustible distillé en vue d'inhiber le dépôt de coke sur les 25 injecteurs de moteurs à allumage par compression à injection indirecte, d'une association entre (a) un accélérateur d'allumage du type d'un nitrate organique et (b) un succinimide ou succinamide à substituant hydrocarbyle et, à titre facultatif:

(c) une hydrocarbylamine ayant 3 à 60 atomes de carbone et 1 à 10 atomes d'azote, ou bien une association formée entre une hydrocarbylamine (c) et (d) le N,N'-disalicylidène-1,2-diaminopropane, l'association étant facultativement telle que défini dans l'une quelconque des revendications 2 à 7.

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